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Synthesis of Poly(L(+) Lactic Acid) by Polycondensation Method in Solution

Abstract
In this work. the results of the synthesis of high molar weight poly(L(+) lactic acid) (PLA) which is able to thermally crystallise have been described. Such PLA can be used in fibre formation. The synthesis of poly(L(+) lactic acid) was carried out in a solution of o-dichlorobenzene, p-xylene, o-chlorotoluene, and diphenyl ether. As a monomer, L(+)lactic acid purified by distillation was applied. Stannous chloride and metallic tin were used as catalysts in a quantity of 1.0 wt% calculated on the monomer. Polycondensation was carried out over a period from ten to over 20 hours. The resulting poly(L(+) lactic acids) were characterised by DSC, and the molar masses were measured by the GPC method. Their melting points, thermostabilities, inherent viscosities, and flow indexes were also determined. The poly(L(+) lactic acid) with the highest molar mass was obtained in the synthesis carried out in diphenyl ether under vacuum.

Key words: *poly(L(+) lactic acid), polycondensation, poylactide.*

◼ Introduction

The production of plastics, and articles produced from them, is expanding systematically. Simultaneously, the amount of waste is increasing because the majority of conventional plastics are resistant to the long-lasting action of weather and/or drastic biological conditions. Both recycling and combustion are processes which permit only a partial solution of the above-mentioned problem. Thus, in recent years we have observed intensive development in investigations into biodegradable polymers. It seems that one polymer which may meet our requirements and replace the majority of popular plastics on the market is poly(L-(+)-lactic acid) (PLA). This assumption confirms the actuation of PLA production by world-famous firms, namely Cargill Dow Polymers (USA) and Mitsui Toatsu Chemicals Inc. (Japan) [1].

Lactic acid (α-hydroxypropionic acid), used as a substrate in the synthesis of PLA, belongs to the hydroxyacids. Hydroxyacids are characterised by greater acidity than acids devoid of hydroxy groups, because the presence of hydroxy groups (particularly in the α position) considerably facilitates the dissociation of carboxyl groups. For this reason α-hy-droxypropionic acid is ten times stronger than propionic acid [2].

CH_3CH_2COOH pK_a=4.9
$CH_3CH(OH)COOH$ pK_a=3.9
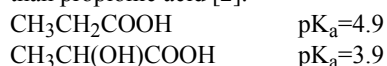
Lactic acid contains one asymmetric carbon atom, and it therefore occurs in two enantiomeric forms. In the technological synthesis of poly(lactic acid), this dextro-rotatory enantiomer (L(+) lactic acid) is mostly used, which gives the crystalline poly(L(+) lactic acid) (PLA). A mixture of enantiomers of lactic acid is applied in the food and tanning industries. The commercial lactic acid (LA), available as an 85-92% aqueous solution, contains an admixture of the linear dimer $CH_3CH(OH)COOCH(CH_3)COOH$, i.e. laktyllactic acid, which is formed during the concentration of LA under atmospheric pressure. During the heating of laktyllactic acid to the temperature of 180-250°C, dehydratation occurs and the cyclic diester-lactide is formed [3]. Lactide can occur in two optic active enantiomers, a racemic mixture and in mezo form [4].

L(+) and D(−) lactic acids, as a consequence of the presence of the hydrogen atom connected to an asymmetric carbon atom, can undergo enolisation, [3] which in turn leads to autoracemisation, that causes a loss of the optical activity of the initial acid (Figure 1).

Poly(L(+) lactic acid) (PLA) is synthesised by two methods: (1) the polymerisation of L-lactide (cyclic dimer of lactic acid) and (2) the polycondensation of L(+) lactic acid (LA), which is carried out in bulk or in solution. So far, the synthesis of PLA from lactide is the best-known method of synthesis. This process is used in industry and numerous publications and patents are devoted to it. The direct polycondensation of lactic acid in bulk is not applied on a greater scale, because of the competitive reaction of lactide formation and the simultaneously occurring degradation process. The polycondensation of lactic acid in solution gives PLA with molar masses ranging from the tens to a few hundred thousand. This process has been well known since 1994. The outstanding achievements in this field belong to Japanese scientists [6-8]. In their works, L(+) lactic acid from Purac without prior purification was used as the starting material in polycondensation. In the present work, we used as a substrate L(+) lactic acid from Fluka which had been purified by distillation. In polycondensation carried out in p-xylene and diphenyl ether, lower molar masses of PLA were obtained than that reported by the Japanese authors in
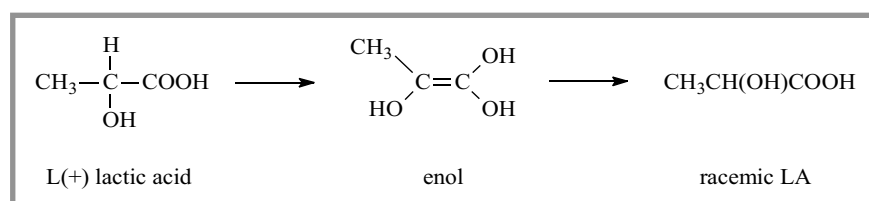

Figure 1. Racemisation of lactic acid.

analogous syntheses. The polycondensation of L(+) lactic acid in o-dichlorobenzene and o-chlorotoluene was carried out under atmospheric pressure and has not so far been described in the literature.

The PLA obtained in the polymerisation of lactide and/or in the polycondensation of LA in the solution is constructed from identical structural units. Both polymers have only different end-groups that influence some of their physico-chemical proprieties [6,8].

The main aim of this work was to obtain high molar mass poly(L(+) lactic acid) with a high degree of crystallinity that makes it useful in fibre formation.

■ Experimental Part

Reagents

L(+) lactic acid containing 10-15% of water (Fluka, Swotzerland).
The following solvents were used without purification:
- diphenyl ether (DPE) (Aldrich) - purity 99%;
- o-chlorotoluene (o-ChT) (Aldrich) - purity 99% (GC);
- o-dichlorobenzene (o-ChB) (Aldrich) - purity 99% spectrophotometric grade;
- p-xylene (p-Xy) (Aldrich) - 99% HPLC grade;
- chloroform, pure (PPH 'POCh' S. A., Gliwice);
- methanol, pure (PPH 'POCh' S. A., Gliwice).

In addition:
- molecular sieves 4A, Chemiczne Przedsiebiorstwo 'Reagents' Spólka z.o.o. Lublin;
- stannous chloride anhydrous (Fluka) and powdered tin (for analysis) (SERVA) - the grain size of <0.01 mm were used as received.

Description of PLA samples

In this work polymer samples of the following description were applied: letters denotes the solvent in which the synthesis of PLA was carried out, and the numbers refer to the time of reaction, e.g. DPE-28 denotes that PLA was obtained in diphenyl ether in 28 hours.

Purification of lactic acid

The commercial lactic acid was dehydratated during heating under vacuum (~15 mm Hg) at a temperature of 50°C. The heating was stopped when the temperature reached 70°C (without changing the pressure). Then the apparatus was desiccated, and the residue was distilled under vacuum (10 mm Hg) at a temperature of 112-136°C.

It should be noted that in conditions of distillation of L(+) lactic acid, side products of this polycondensation may be formed, e.g. laktyllactic acid, which could contaminate the distillate. Therefore in the next part of this work, the distilled L(+) lactic acid will be referred to as 'the product of distillation of L(+) lactic acid'.

Synthesis of poly(L(+) lactic acid)

Polycondensation of LA in solution under atmospheric-pressure

80 g of the product of distillation L(+) lactic acid was dissolved in 300 mL of o-dichlorobenzene in a three-necked flask (0.5 dm³). 0.8 g of metallic tin (grain size

Table 1. Influence of the conditions of reaction on thermostability PLA.

Sample	Decrease of polymer mass during the first two hours heating (in wt%)	
	160°C	180°C
p-Xy - 37	1.6	6.8
o-ChB - 20	2.8	18.8

~0.01 mm) was added to this solution, and the reaction mixture was heated. The water was azeotropically distilled off, and fresh solvent was added during the distillation to keep the reagent concentration constant. The reaction was carried out until a clear distillate appeared in the receiver. Then a tube packed with 40-50 g of 4Å type dry molecular sieves was mounted onto the apparatus, and the reaction was continued at 180°C for several hours in a closed circulation system for the solvent. During the synthesis the control samples were taken out, until the reaction mixture attained the maximum viscosity.

Then the metallic tin was filtered off, and the resulting solution was poured into an excess of methanol (of five times greater volume). The resultant white powder was washed several times with methanol and dried at 80°C for 2 h. The final product, called further poly(L(+) lactic acid, was not additionally purified before analysis of its physico-chemical properties.

Syntheses in p-xylene and in o-chlorotoluene were carried out analogously at temperatures of 138°C and 159°C respectively. In the case of the reaction in p-xylene, stannous chloride was used as a catalyst in the quantity of 1 wt% (calculated on the amount of monomer). It was dissolved in methanol during the precipitation of PLA.

Polycondensation of LA in solution under reduced pressure

85 g of the product of distillation L(+) lactic acid was dissolved in 400 mL of p-xylene in a four-necked flask (0.5 dm³). 0.85 g of metallic tin (grain size ~0.01 mm) was added to this solution, and the reaction mixture was heated at 136°C to remove azeotropic water, until a clear distillate appeared in the receiver. Then, the p-xylene was removed under reduced pressure (~300 mm Hg) at temperature not exceeding 146°C. Next, 250 mL of diphenyl ether was added and the reaction mixture was heated at 130°C under vacuum (12-15 mm Hg). The process
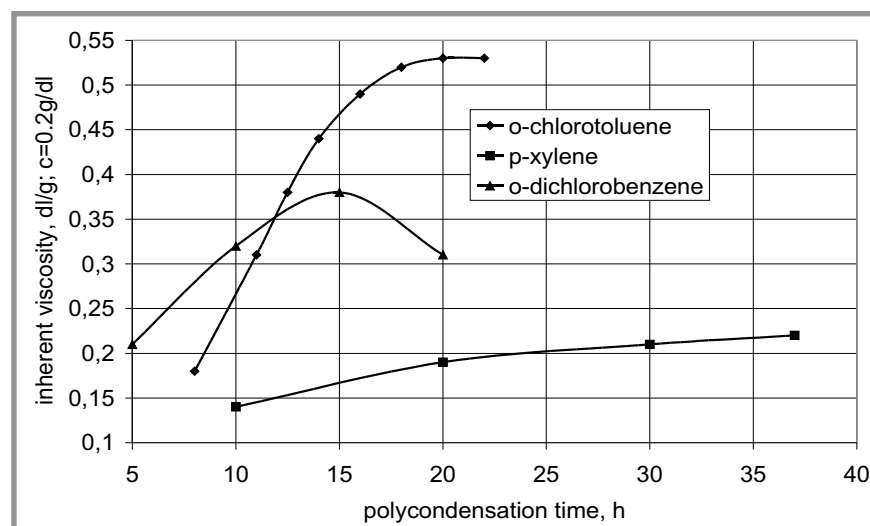

Figure 2. Influence of polycondensation time on inherent viscosity of PLA.

was carried out in a closed system and the circulated solvent removed residual water from the reaction mixture. Water was absorbed by molecular sieves placed in the receiver, as described in the previous example. The procedure of isolating the resulting products was similar to that described above.

Analysis of products

Determination of molar masses by GPC method

The polymers' molar masses were determined by the GPC method on a Type 1050 Hewlett Packard chromatograph with an HP 1047A RI detector in chloroform as a mobile phase at a flow rate of 1.0 mL×min^{-1}. One Pl gel Mixed D column (7.8×600 mm; 5 µm; Polymer Laboratories Ltd.) was used for determination. The samples (concentration of polymers: 3 mg/mL) were filtered through 0.2 µm-pore size membrane filters. The injection volumes of the sample solution were 70 µl. The calibration of the column was performed with narrow polystyrene standards.

Determination of melting points

The melting points of the resulting PLA were determined on Boëtius (Nagema) apparatus.

DSC measurements

The DSC measurements were carried out under a nitrogen atmosphere with samples sealed into the standard DSC aluminium sample kits. The following thermal cycle was employed:
First, sample I was heated up to a temperature about 20°C above the melting point; next, cooled down to about 10°C; then, sample II was heated up to the same temperature as in the first stage. The samples investigated had weights within the range of 5 to 15 mgs. Both heating and cooling rates were 20°C/min.

Measurements of thermal stability

Measurements of the thermal stability of PLA were performed on a TGS -1 thermobalance with a UK -1 (Perkin-Elmer) temperature programmator unit at a heating rate of 10°C/min and under a nitrogen flow of about 30 mL/min. The analysis of thermostability of PLA samples, obtained in the syntheses in p-xylene (140°C) and in o-dichlorobenzene (180°C), was performed at temperatures of 160°C and 180°C respectively.

Viscosity measurements

Viscosity measurements were performed in chloroform at a temperature of 25°C in an Ubbelohde viscometer with capillary 0a and K=0.00498. Inherent viscosity was calculated according to the following equation:

$$\eta_{inh} = \ln \eta_{rel} / c$$

where:
η_{rel} - relative viscosity,
c - concentration of polymer, g/dl.

Determination of flow index

Determination of flow indexes were performed on a Melt Flow Tester apparatus of type P/N 6941.000 (CEAST) using a load of 2.16 kg and a spinneret of 0.5 mm.

■ Results and Discussion

In this work the synthesis of PLA was carried out in chemically different solvents and at various temperatures. Metallic tin and stannous chloride were used as catalysts in quantity of 1 wt%, calculated according to the amount of monomer. The progress of the polycondensation of L(+) lactic acid in solution was controlled by regular sampling small amounts from the reaction mixture and determining the viscosity of the isolated poly(lactic acid). In every synthesis we tried to obtain PLA with the highest molar mass.

Synthesis of PLA in p-xylene was carried out in the presence of stannous chloride as a catalyst at 138°C. After 20 h of heating, the molar mass of the resulted polymer increased insignificantly, and after 37 h of the reaction the resulting polymer had η_{inh}=0.22 dl/g and m.p.=163°C.

Synthesis of PLA in o-dichlorobenzene in the presence of metallic tin proceeded with considerably higher speed in comparison to that with p-xylene because of the significantly higher reaction temperature (159°C). PLA with the highest viscosity was obtained after 15 h of polycondensation. The samples for viscosity determination were in this case taken at rather large intervals (every 5 h), and so the plot viscosity vs. time of polycondensation (Figure 2) should be considered as approximation. On the other hand, the presence of thermodegradation was observed because of the high temperature process (cf. Table 1). It can therefore be assumed that the maximum of the resultant PLA's viscosity should be reached between 13 and 18 h of the process. The melting point T_m of polymer after 20 h of polycondensation was equal to 130-132°C.

Samples obtained in different solvents, o-ChB-20 (at 180°C in o-dichlorobenzene after 20 h) and p-Xy-37 (at 140°C in p-xylene after 37 h), were subjected to thermal stability analysis after being dried to the constant mass at 120°C. The loss of mass of the polymers analysed over two hours at temperatures of 160 and 180°C is shown in Table 1.
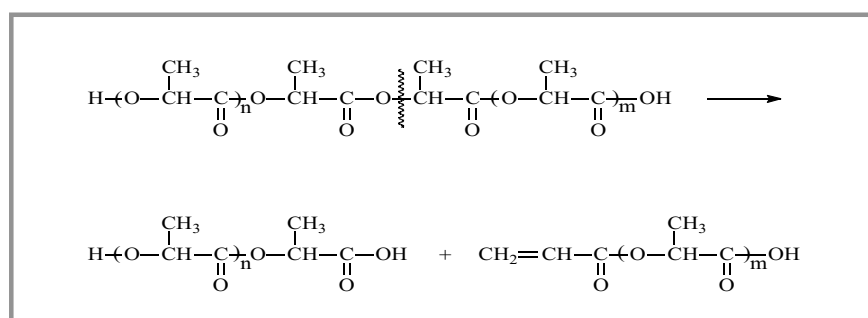

Figure 3. *Thermal break-up of PLA chain upon the formation of molar mass stabiliser.*
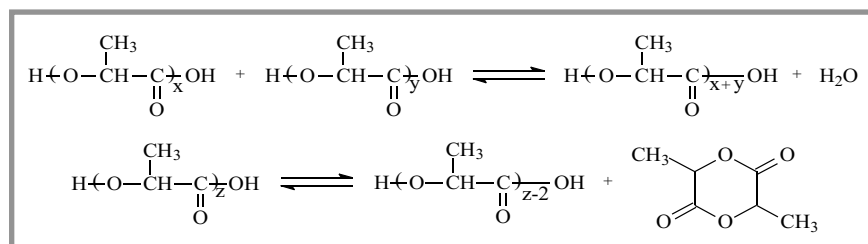

Figure 4. *Equilibria observed during polycondensation of LA: PLA - H₂O and PLA - lactide.*

It has been found that the lower temperature of PLA synthesis favours the formation of polymers with higher thermal stability and molar mass, and with lower tendency to create by-products. The fast growth observed in the molar mass, and then its fall during polycondensation in o-dichlorobenzene, may be connected with the formation of molar mass stabiliser as a result of the thermal rearrangement of PLA.

One possible way to thermodegrade PLA is the thermal break-up of the ester bond upon formation of the acidic stabiliser of molar mass (Figure 3) [9].

For the synthesis performed under atmospheric pressure, the highest viscosity of polymer was obtained in the polycondensation carried out in o-chlorotoluene (o-ChT-22) (Figure 2). The molar masses M_n and M_w of this polymer, as determined by the GPC method, were equal to 2.6×10^4 and 6.7×10^4 respectively.

All syntheses were performed with drying solvent during the process and its circulation in the closed system. This is of essential significance for the progress of polycondensation, despite the equilibrium process of PLA formation [10] (Figure 4).

Polycondensation of L(+) lactic acid under reduced pressure (12-15 mm Hg) was performed in diphenyl ether at 130-135°C. As a result, two poly(L(+) lactic acids) DPE-27 and DPE-36, after 27 and 36 h of the reaction, were obtained respectively. Their physicochemical properties, especially their low flow indexes at 180 and 190°C (cf. Table 2), were better than for the other polymers previously obtained.

Poly(L(+) lactic acids) showed fibre-forming properties and threads were successfully formed from them. The best thermostability in melt was shown by DPE-36. The differences of its flow indexes, after 30 minutes and after 6 minutes at 180 and 190°C, were not great, and were equal to 0.49 and 2.45 respectively (cf. Table 2), which is the important parameter in the process of fibre formation. When fibres are spinning from the melt, the time which the polymer spends in the apparatus in the melting state is considerably shorter, and it lasted not more than 12 minutes.

The M_n of PLA as determined by the GPC varied from 2.6×10^4 to 4.0×10^4

(determined for polystyrene standards). Poly(L(+) lactic acids) with the above-mentioned physico-chemical properties could be successfully used in the production of semi-finished articles and final products such as cast profiles, foils, packaging, and fibres.

Figure 5 shows the dependence of inherent viscosity vs. M_n and M_w of PLA samples from Table 2. Point $\eta_{inh}=0.7$ (in Figure 2) corresponds to the control sample of polymer removed after 22 h during the synthesis of DPE-36.

According to some authors [11], PLA with $M_n \approx 25 \times 10^4$ already has reasonable physical proprieties for commercial use.

The essential, valuable property of polymers designed for fibre formation is the ability to regenerate, after melting, the

crystalline phase during cooling (crystallisation from melt) or during repeated heating of polymer (the cold crystallisation). Table 3 shows three samples of PLA, o-ChT-22, DPE-27, and DPE-36, which were obtained after different heating times (22, 27, and 36 h) in o-ChT (at 159°C) and DPE (at 130°C). In the DSC measurements during the second heating, it was observed that DPE-27 reproduces a considerable part of crystalline phase, whereas DPE-36 reproduces only a minimum part, and o-ChT-22 remains amorphous.

The melting points of DPE-27 and DPE-36 samples (cf. Table 3), as determined by the DSC method, differ only slightly from the values reported in the literature for poly(L(+) lactic acid) synthesised by the polycondensation method in solution [6]. The melting point of o-

Table 2. *Inherent viscosity and Melt Flow Index for some samples of PLA.*

Sample	η_{inh}, dl/g		MFI, g/10 min			
			180°C		190°C	
	c=0.1 g/dl	c=0.2 g/dl	after 6 min	after 30 min	after 6 min	after 30 min
o-ChT-22	0.53	0.53	14.94	29.75	21.56	-
DPE-27	0.94	1.01	0.97	4.25	2.52	17.81
DPE-36	0.87	0.92	0.61	1.10	0.93	3.38

Table 3. *Thermal properties of some samples of PLA (T_g - glass transition temperature, $T_{cc}/\Delta H_{cc}$ - cold crystallisation temperature/enthalpy, $T_m/\Delta H_m$ - melting temperature/enthalpy, $T_c/\Delta H_c$ - melt crystallisation temperature/ enthalpy, n.d. - not detected, I/II - first/second heating).*

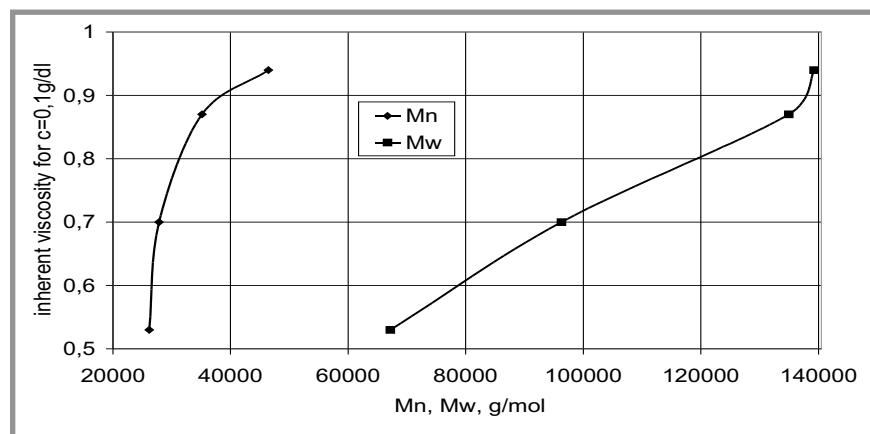| Sample		Heating, 20°C/min					Cooling, 20°C/min		
		T_g, °C	T_{cc}, °C	DH_{cc}, J/g	T_m, °C	DH_m, J/g	T_c, °C	DH_c, J/g	T_g, °C
o-ChT-22	I	61.5	n.d.	n.d.	151	48.5	n.d.	n.d.	57
	II	58	n.d.	n.d.	151	0.36	-	-	-
DPE-27	I	56	n.d.	n.d.	161	59.2	n.d.	n.d.	59.5
	II	59	136	9.0	165	9.3	-	-	-
DPE-36	I	~58	n.d.	n.d.	158	52.6	n.d.	n.d.	58.5
	II	58.5	134	2.2	162	1.5	-	-	-

Figure 5. *Dependence between inherent viscosity and molar masses of PLA samples.*

TEXTILES & HEALTH SCIENTIFIC NETWORK

The **Polish Textiles & Health Scientific Network (TEXMEDECO NET)** was established as an initiative of the **Textile Research Institute, Łódź, Poland (Instytut Włókiennictwa - IW)** and other R&D centres which are active in the area of:
• MED-TEXTILES: textiles for medical treatment,
• ECO-TEXTILES: textiles safe for human health,
• ENVIRO-TEXTILES: textiles protecting against physical, chemical and biological hazards.

The 1st group covers all textile fabrics assisting medical treatment and prophylaxis. (textile dressings, antibacterial fabrics, textile prostheses and implants, and modern intelligent textiles applied in medical diagnostics and treatment).

The 2nd group covers research works and studies aiming at protecting human (skin, respiratory and thermoregulating systems) against negative effects of textile fabrics.

The 3rd group comprises textile fabrics protecting humans against harmful effects of external factors (electromagnetic and electrostatic fields, UV and IR radiation, microorganisms).

The TEXMEDECO NET was registered on the basis of a formal decision of the Ministry of Scientific Research and Information Technology in Warsaw on 31.01.2003.
The Network's primary goals:
• integration of R&D centres into the network's activity (local and international levels),
• utilisation of integrated R&D achievements in scientific co-operation .
• network development - modification or integration with European Networks,
• inclusion of scientific potential in thematic consortia created in European Union, also within the 6th Framework Programme of European Union.

These goals should be accomplished through:
• preparation - on the level of Network Work Groups - of own thematic proposals for mutual research projects,
• organising own conferences or seminars to promote achievements of network member institutions and to stimulate research contacts in Poland and abroad,
• getting into contacts with existing in the UE scientific networks acting in the similar field,
• integration of member institutions activities to respond to the calls of the 6th Framework Programme of European Union,
• search for new partners in Poland and abroad to work together within the network's scope.

The TEXMEDECO NET comprises 18 R&D institutions (www.iw.lodz.pl) covering the following areas: textiles, medicine, occupational medicine and leather industry.
The IW acts as the Network's coordinating institution, represented by Jadwiga Sójka-Ledakowicz, Ph.D., Eng., the network coordinator.

The following bodies form the Network structure: General Assembly, Steering Committee and Work Groups (Med-, Eco and Enviro-Textiles) which act on the basis of the Statute and specific Regulations.

The annual TEXMEDECO NET CONFERENCE is the forum of information exchange and presentation of scientific achievements of network members.

The TEXMEDECO NET has an open character. R&D institutions of different state, scientific and technical organisations, producers (SME), and others representing various disciplines can have their contribution in network activities.

We welcome any new members both from Poland and abroad !!!
Interested parties should contact the Network Coordinating Office:
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ChT-22 differs considerably from the values given in literature. That difference can probably be explained by the high temperature of polycondensation in this solvent, which causes the partial racemisation of the resulting polymer [7,8]. The glass transition temperatures of studied poly(lactic acids) agree with the literature data [6].

■ Conclusion

The best results of polycondensation of L(+) lactic acid in solution were obtained using diphenyl ether as the solvent. The temperature of the synthesis of poly(L(+) lactic acid) should not exceed 140°C; at higher temperatures racemisation can occur. The poly(L(+) lactic acids) obtained in diphenyl ether showed fibre-forming properties.

In recent years the whole world has seen great interest in improving the methods of synthesising poly(L(+) lactic acid) and the products of its processing. In the near future PLA may have the opportunity to substitute the popular plastics, and so further intensive investigation into the polycondensation of lactic acid in solution should be carried out.

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